Near-quantitative Removal of Oxalate and Terephthalate from Water by Precipitation with a Rigid Bis-amidinium Compound

Rosemary J. Goodwin,[a] Phonlakrit Muang-Non,[a] Nikki A. Tzioumis,[b] Katrina A. Jolliffe[b] and Nicholas G. White*[a]

[a] *Research School of Chemistry, Australian National University, Canberra, ACT, 2601, Australia. Email: nicholas.white@anu.edu.au, Web: www.nwhitegroup.com*

[b] *Australian Research Council Centre of Excellence for Innovations in Peptide and Protein Science, School of Chemistry, The University of Sydney, Sydney, NSW, 2006, Australia*

A simple, readily-prepared precipitant (**1·Cl₂**) precipitates oxalate or terephthalate from water with very high efficacy, removing these anions at sub-millimolar concentrations using only one equivalent of precipitant. A simple aqueous base/acid cycle can be used to regenerate **1·Cl₂** after use. The resulting precipitates, **1·oxalate** and **1·terephthalate**, are anhydrous and closely-packed, with each anion receiving eight charge-assisted hydrogen bonds from amidinium N–H donors. Precipitation of oxalate and terephthalate occurs at much lower concentrations than other dicarboxylates, and direct competition experiments with the biologically/environmentally relevant divalent anions CO_3^{2-}, HPO_4^{2-} and SO_4^{2-} reveal very high selectivity for oxalate or terephthalate over these competitors.

Introduction

Anions are of vital importance in numerous biological, environmental and industrial processes, and so the development of anion receptors and sensors is a major focus of supramolecular chemistry.[1–3] Achieving anion recognition in water is notoriously difficult as both hosts and the majority of anions have high hydration enthalpies and so interactions with the solvent typically outcompete host–guest interactions.[4] Even when anion binding can be achieved in water,[5–14] doing this selectively is extremely challenging, and where selectivity has been achieved it tends to be either selectivity for more highly charged anions over less charged ones (electrostatics-driven)[15,16] or for more lipophilic anions over hydrophilic ones (hydrophobicity-driven).[6,17,18] Achieving selectivity between similar anions in water thus remains a largely unsolved challenge.

One possible approach to achieving selectivity between similar anions in water is to use precipitation instead of recognition in solution. While this is not possible in every situation, if it can be used then subtle differences in solubility and crystal packing may lead to selectivity where one anion is just insoluble enough to begin to crystallise while others remain in solution. Precipitation also has the added advantage of removing the anion from the medium potentially allowing for clean-up of contaminated water.

A significant body of research has investigated selective precipitation of sulfate from water: while simple metal ions such as barium are effective sulfate precipitants, they suffer from a lack of selectivity.[19] Early studies investigated simple organic precipitants although these suffered from low solubilities of the precipitant and limited selectivity.[20–22] In 2015, Custelcean reported readily-prepared bis-iminoguanidinium compounds (**BIG**$^{2+}$, Figure 1) that are effective sulfate precipitants and showed good selectivity against relevant anions such as Cl^- and NO_3^-.[23] Since then, a small family of these systems have been described. Interestingly sulfate is always precipitated in hydrated form (two to five water molecules per anion).[23–25] Very recently, Einkauf and Custelcean reported that these **BIG**$^{2+}$ precipitants could also precipitate selenate and selenite anions: while no selectivity was observed between the very similar sulfate and selenate anions, > 99% of sulfate and/or selenate could be removed by using an excess of precipitant.[25]

Inspired by Custelcean's work, we recently reported that the simple bis-amidinium compound **1**$^{2+}$ could remove > 95% of sulfate from aqueous solution and was selective for this anion even in the presence of competitive divalent anions.[26] Like Custelcean's precipitants,[23–25] **1**$^{2+}$ could be regenerated for subsequent reuse. Even though the structure of **1**$^{2+}$ is relatively similar to that of the **BIG**$^{2+}$ precipitants, different crystallisation behaviour is observed with **1**$^{2+}$ precipitating anhydrous sulfate while **BIG**$^{2+}$ compounds precipitate hydrated anions. In the current work, we extend our studies to look at the precipitation of dicarboxylate anions, as these are known to be important in biology and industry.[27,28] Specifically, we demonstrate that oxalate and terephthalate (*i.e.* 1,4-benzenedicarboxylate) can be removed from water with high efficiency at low concentrations. While impressive systems for binding and sensing oxalate[29,30] and terephthalate[31,32] in water have been reported, we are unaware of any reports of selective precipitants for these anions.

These anions are not found at significant concentrations in natural systems such as waterways. However, oxalate is toxic,[28] is problematic for industrial bauxite processing,[33] and has been suggested as a mechanism for carbon storage,[34,35] while tens of millions of tons of terephthalate are produced annually during production (and sometimes recycling) of PET plastics.[36] While the focus of the current work is on understanding selective precipitation processes, we believe that these kinds of precipitants could prove useful in remediation of industrial spills of oxalate and terephthalate.

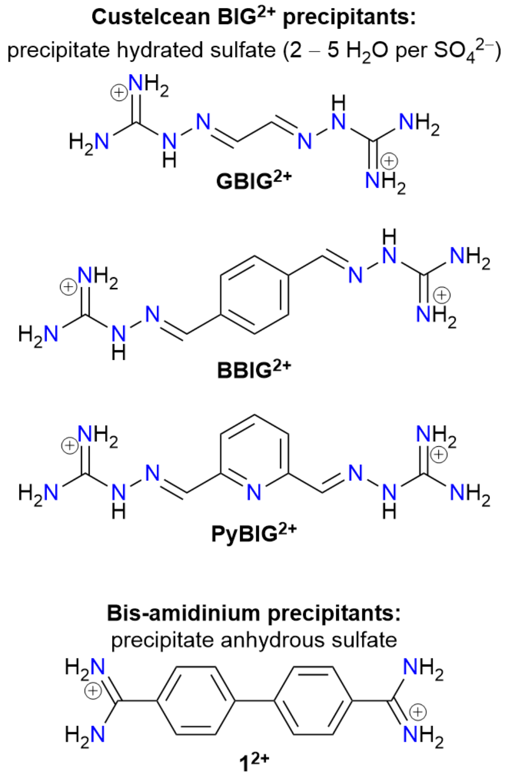


Figure 1 Dicationic sulfate precipitants reported by Custelcean's group[23–25] and our group.[26]

Results and discussion

Precipitation of polycarboxylates

We have previously tested the ability of **1·Cl$_2$**, which is highly water soluble (> 50 mM), to precipitate monovalent anions, HPO_4^{2-}, carbonate and sulfate.[26] We found that **1·Cl$_2$** precipitated sulfate with complete selectivity over monovalent anions, and was effective at concentrations as low as 1.0 mM, but did not precipitate sulfate at 0.50 mM. When **1·Cl$_2$** was exposed to a mixture of sulfate and carbonate, **1·sulfate** precipitated selectively with no evidence of carbonate precipitation.

In the current work, we have expanded this study to look at a range of dicarboxylate anions, as well as citrate. We initially mixed equal volumes of 20 mM aqueous solutions of **1·Cl$_2$** and the sodium salt of the anion of interest to give final solutions with concentrations of 10 mM of **1**$^{2+}$ and the di/tri-carboxylate of interest. All studied carboxylates (citrate, malonate, oxalate, succinate, terephthalate) formed immediate precipitates upon mixing with **1**$^{2+}$ at these concentrations. We next conducted similar studies at lower concentrations until no precipitation was observed. These results are presented in Table 1, along with a summary of our previously-reported results.

Table 1. Time taken for visible precipitation when mixing **1·Cl$_2$** and anions at various concentrations.

Anion	10 mM [a]	2.0 mM [a]	1.0 mM [a]	0.50 mM [a]	0.25 mM [a]	0.10 mM [a]
$Cl^-/Br^-/I^-/NO_3^-/ClO_4^-/HCO_3^-$ [26]	no ppt.[b]	–	–	–	–	–
HPO_4^{2-} [26]	~ 5–10 s	no ppt.[b]	–	–	–	–
carbonate^{2-} [26]	~ 5–10 s	several hours	no ppt.[b]			
malonate^{2-}	immediate	~ 15 hr	no ppt.[b]	–	–	–
citrate^{3-}	immediate	several hours	no ppt.[b]	–	–	–
succinate^{2-}	immediate	~ 1 hr	~ 15 hr	no ppt.[b]	–	–
sulfate^{2-} [26]	immediate	~ 15 s	several hours	no ppt.[b]	–	–
oxalate^{2-}	immediate	~ 1 min	several hours	several hours	no ppt.[b]	–
terephthalate^{2-}	immediate	immediate	5–10 s	~ 5 min	~ 15 min	~ 24 hours

[a] Concentration refers to final concentration of both **1**$^{2+}$ and anion after mixing. [b] No precipitate observed within 24 hours.

At a concentration of 1.0 mM, no precipitation was observed within 48 hours for malonate or citrate (we have previously shown that carbonate and HPO_4^{2-} also do not precipitate at this concentration[26]), while relatively rapid precipitation was observed for terephthalate, and slower precipitation for sulfate, succinate, and oxalate. At 0.50 mM, only oxalate and terephthalate precipitated with significant precipitation of both **1·oxalate** and **1·terepthalate** at this concentration. In the case of **1·terephthalate**, precipitation was observed at concentrations as low as 0.10 mM. All of the precipitated solids containing carboxylate anions could be obtained as single crystals and were characterised by SCXRD and PXRD studies, as well as NMR analysis of digested crystals, thermogravimetric analysis, IR spectroscopy and elemental analysis (see later for discussion of crystal structures, and SI for characterisation).

Given the effective precipitation of oxalate and terephthalate by **1·Cl$_2$**, we conducted bulk precipitation studies at a range of concentrations, ranging from 2.0 to 20 mM. These studies were conducted on either 1.00 or 3.00 mmol scales (see SI for full details). At 10 mM and 20 mM concentrations, near-quantitative removal (95 – 98%) of oxalate and terephthalate was observed (Table 2), as was previously observed with sulfate.[26] At lower concentrations (2.0 and 5.0 mM), removal was still near-quantitative (≥ 95%), which contrasts with previously-reported results for sulfate, where yields decreased at these lower concentrations.[26]

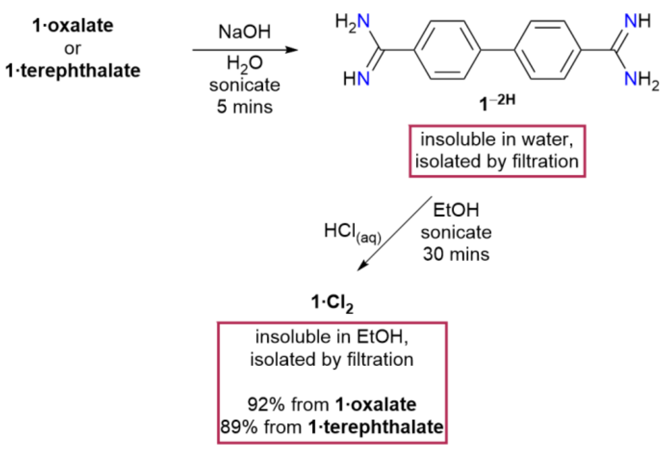
Table 2. Yields of **1·oxalate**, **1·terephthalate** or **1·SO$_4$** precipitated from equimolar mixtures of aqueous **1·Cl$_2$** and sodium oxalate, terephthalate or sulfate.

Concentration (mM) [a]	1·oxalate yield (%)	1·terephthalate yield (%)	1·SO$_4$ yield (%)[26]
20	98	97	not determined
10	98	95	96 [26]
5.0	99	95	92 [26]
2.0	97	95	78 [26]

[a] Concentration of both **1**$^{2+}$ and anion.

Regeneration of 1·Cl$_2$

We have previously reported that **1·Cl$_2$** can be regenerated from **1·SO$_4$** using either $BaCl_2$, or treatment with $NaOH_{(aq)}$ to generate the neutral bis-amidine (**1**$^{-2H}$) followed by regeneration of **1·Cl$_2$** using HCl.[26] This procedure, outlined in Scheme 1, is based on a similar approach used by Custelcean for bis-guanidinium **BIG**$^{2+}$ precipitants.[24] In our initial report, this basification/acidification procedure gave an unoptimised 78% yield of recovered **1·Cl$_2$**. We investigated the basicification/acidification approach to regenerate **1**$^{2+}$ from **1·oxalate** and **1·terephthalate**, and optimised the procedure to increase the recovery. This gave **1·Cl$_2$** as expected, and after optimisation we were able to recover this compound in ~90% yield. This procedure is given in the Supporting Information, but it was important to minimise both the amount of time that **1·oxalate** or **1·terephthalate** was exposed to the basic solution (due to the instability of amidines in the presence of aqueous base[37]) as well as the amount of solvent/$HCl_{(aq)}$ used in the re-acidification step to avoid losses due to **1·Cl$_2$** dissolving.



Scheme 1 Regeneration of **1·Cl$_2$** from **1·oxalate** and **1·terephthalate**. The sodium oxalate and sodium terephthalate generated in the initial NaOH step are soluble in water and stay in solution. Small amounts of impurities that precipitate with **1**$^{-2H}$ stay in the ethanol/$HCl_{(aq)}$ solution so pure **1·Cl$_2$** is recovered.

Thermodynamics of crystallisation

We determined the aqueous solubilities and solubility products of **1·oxalate** and **1·terephthlate** and compared this with our previously-reported value for **1·SO$_4$** [K_{sp} value of $9(1) \times 10^{-8}$].[26] The K_{sp} values for **1·oxalate** and **1·terephthalate** [$1.6(2) \times 10^{-9}$ and $1.8(1) \times 10^{-10}$] are notably lower than that previously reported for **1·SO$_4$**, and indeed the K_{sp} value for **1·terephthalate** is comparable to that of other notoriously insoluble salts such as AgCl and $BaSO_4$ (K_{sp} values of 1.8 and 1.1×10^{-10},[38] respectively). In contrast, the solubilities for the other carboxylate anions are substantially higher than **1·oxalate** and **1·terephthalate**: $5.4(2) \times 10^{-7}$, $1.6(1) \times 10^{-7}$ and $2.5(1) \times 10^{-8}$ for **1·carbonate**, **1·malonate** and **1·succinate**, respectively.

Van't Hoff analysis of variable temperature solubility data (see Supporting Information) indicates that crystallisation is enthalpically and entropically favourable for **1·oxalate**, **1·sulfate** and **1·terephthalate** (Table 3). For **1·oxalate** and **1·sulfate**, enthalpy is the more significant driver representing about ¾ of the energetic favourability, while for **1·terephthalate** the entropic term is more substantial. Generally, these values are quite similar to one another, which contrasts with data for **BIG**$^{2+}$ precipitants with SO_4^{2-}, SeO_4^{2-} and SeO_3^{2-} where ΔH values range from −20 to −152 kJ mol^{-1} and TΔS values ranged from −104 to + 133 kJ mol^{-1}.[25] We suggest that the greater degree of similarity in our results likely arises from the very similar molecular structures of **1·SO$_4$**, **1·oxalate** and **1·terephthalate** (see later), and the fact that they are all anhydrous structures, whereas **BIG**$^{2+}$ precipitants exist as hydrated anion complexes with varying numbers of water molecules.[23–25]

Table 3. Thermodynamic parameters of crystallisation calculated using van't Hoff analysis. Estimated standard errors given in parentheses.

	ΔH (kJ mol^{-1})	TΔS at 298 K (kJ mol^{-1})	ΔG at 298 K (kJ mol^{-1})
1·oxalate	−35(1)	−13	−48
1·sulfate	−31(1)	−9	−40
1·terephthalate	−15(4)	−36	−52

Competition studies

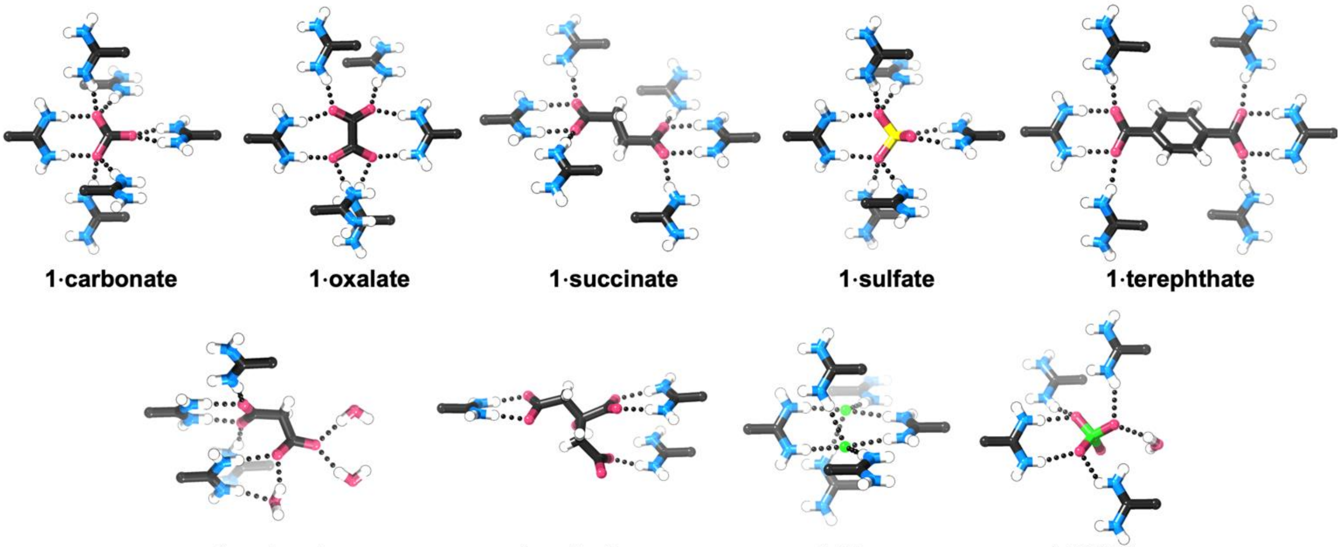
The solubility data indicate that **1**$^{2+}$ can remove extremely low levels of oxalate and terephthalate, and that it is effective at even lower concentrations than for sulfate. We investigated this further by conducting competition precipitation experiments where we mixed aqueous solutions of **1·Cl$_2$** with one molar equivalent of oxalate or terephthalate as well as one molar equivalent each of carbonate, dibasic phosphate, and sulfate. These anions were chosen as they are important biological or environmental anions, and are themselves precipitated effectively by **1**$^{2+}$, so represent rigorous competition. These competition experiments were conducted at both 10 mM and 2.0 mM, with the resulting solids analysed by IR spectroscopy and PXRD (^{1}H NMR analysis of acid-digested solids was not useful due to the absence of ^{1}H resonances in oxalate and peak overlap between **1**$^{2+}$ and terephthalate). In both cases, no evidence of carbonate, HPO_4^{2-} or sulfate incorporation in the precipitated product was observed (see SI for more details).

Further competition experiments for the **1·oxalate** system were conducted using ion chromatography: full results are described in the SI but briefly, solutions with a final concentration of 10 mM of **1**$^{2+}$ and anion(s) were prepared and the concentration of anions remaining in solution after precipitation was analysed. These experiments revealed that the same amount of oxalate was removed (95%, all values given to the nearest 5%) with or without the presence of one equivalent of sulfate, again consistent with highly selective precipitation. In the presence of one equivalent of carbonate or HPO_4^{2-}, a large amount of oxalate was removed (85%) but this was slightly decreased relative to when these competitive guests were absent. Even in the presence of one equivalent each of carbonate, HPO_4^{2-} and sulfate, 80% of oxalate was removed.

X-ray crystal structures of 1^{2+} and anions

We were able to obtain crystal structures of **1·(ClO$_4$)$_2$**, **1$_{1.5}$·citrate**, **1·malonate**, **1·oxalate**, **1·succinate** and **1·terephthalate** in the current work, and we compare these with our previously-reported structures of **1·Cl$_2$**, **1·carbonate** and **1·sulfate** (Figure 2). Crystals of **1·carbonate**, **1·oxalate**, **1·succinate**, **1·sulfate** and **1·terephthalate** are all anhydrous, densely-packed structures and all have very similar hydrogen bonding arrangements. These structures are discussed in more detail later, but briefly each anion receives four charge-assisted hydrogen bonds from "forwards-facing" amidinium N−H donors, and four hydrogen bonds from "sideways-facing" amidinium N−H donors, with these hydrogen bonds being very similar in length across all structures. The structure of **1·Cl$_2$** is also anhydrous and similar to these structures with the two chlorides relatively close together and receiving a similar hydrogen bonding arrangement (although with longer H-acceptor distances due to chloride's larger size and reduced basicity). The structures of **1·(ClO$_4$)$_2$**, **1$_{1.5}$·citrate** and **1·malonate** all contain water solvent molecules. In the structures of **1·(ClO$_4$)$_2$** and **1·malonate**, these water molecules hydrogen bond to the anion, while the structure of **1$_{1.5}$·citrate** is relatively open and appears to contain a large number of water molecules, although the structural data were not of sufficient quality to model the solvent molecules and so PLATON-SQUEEZE[39] was used to include the electron density in the final refinement (see SI for full details).

Hydrogen bonding in densely-packed structures of 1·carbonate, 1·oxalate, 1·succinate, 1·sulfate and 1·terephthalate: These five structures are all anhydrous and densely-packed (crystal densities: 1.44 – 1.54 g cm^{-3}). It is notable that all five of the complexes have relatively low water solubility (< 2.0 mM) and precipitate relatively rapidly (within seconds at 10 mM, within a few hours at 2.0 mM). Kitaigorodskii Packing Indices[40] (KPIs) were calculated using PLATON,[41] and interestingly the structure of **1·sulfate** is notably less densely-packed (KPI = 0.66) than **1·carbonate**, **1·oxalate**, **1·succinate** or **1·terephthalate**, which are quite densely packed (KPIs = 0.72, 0.74, 0.74, 0.76, respectively). We analysed the hydrogen bonding in these related structures in more detail to see if we could observe trends that may shed light on crystallisation behaviour (full details are provided in the SI). While hydrogen atoms are relatively poorly resolved by X-ray crystallography,[42] these five structures are of high quality so we believe that some (cautious) comparisons can be made. In each of these structures, the N−H hydrogen atom positions were refined with restraints on the N−H bond distance.[43]


1·carbonate **1·oxalate** **1·succinate** **1·sulfate** **1·terephthate**

1·malonate **$1_{1.5}$·citrate** **1·Cl$_2$** **1·(ClO$_4$)$_2$**

Figure 2 Portions of X-ray crystal structures showing hydrogen bonding arrangements around anion. The structures of **1·carbonate**, **1·sulfate** and **1·Cl$_2$** have been reported previously.[26] The five structures on the top row are all anhydrous densely-packed structures with similar hydrogen bonding arrangements. Disorder in the structures of **1·malonate** and **1·(ClO$_4$)$_2$** has been omitted for clarity. PLATON-SQUEEZE was used in the refinement of **$1_{1.5}$·citrate**.[39]

Each anion receives eight hydrogen bonds from four "forwards-facing" and four "sideways-facing" amidinium N–H donors, and in some cases additional much longer C–H donors. Hydrogen bonds from the forwards-facing N–H donors have H⋯O distances ranging from 1.86 – 2.01 Å (69 – 74% of the sum of the van der Waals radii[44] of H and O), while those from the sideways-facing N–H donors have H⋯O distances ranging from 1.88 – 2.19 Å (70 – 81% of the sum of the van der Waals radii[44] of H and O). Where C–H hydrogen bonds are present, these are much longer (H⋯O distances: 2.48 – 2.68 Å, 92 – 99% of the sum of the van der Waals radii[44] of H and O). There seems to be some trade-off in hydrogen bonding arrangements, presumably caused by geometrical factors; for example, the structure with the shortest forwards-facing hydrogen bonds (**1·terephthalate**) has the longest sideways-facing hydrogen bonds.

Given the similar hydrogen bonding arrangements in the five structures, and to allow comparison between structures, we averaged all the N–H⋯O hydrogen bonds in each structure. The shortest mean H⋯O distance is found in the structure of **1·carbonate** (1.94 Å), while the longest is found in the structure of **1·sulfate** (2.01 Å), with the dicarboxylate anions oxalate, succinate and terephthalate having intermediate values (1.97 Å, 1.98 Å, 2.00 Å, respectively). Shorter hydrogen bonds do not appear to be correlated with reduced solubility, as the salt with the shortest hydrogen bonds (**1·carbonate**) is the most soluble. As expected,[45] hydrogen bond lengths instead seem to be correlated with basicity, with relatively good correlation between the p*K*a of the conjugate base of each anion and hydrogen bond length (Figure S64).

Other bis-amidiniums

We previously investigated the ability of the smaller and larger bis-amidinium compounds 2^{2+} and 3^{2+} (Figure 3) to precipitate sulfate.[26] Compound 2^{2+} has high water solubility as its chloride salt (~ 150 mM) but is a poor sulfate precipitant (no precipitation at 10 mM). Compound 3^{2+} could precipitate sulfate at very low concentrations (0.10 mM) but was poorly soluble as its chloride salt (~ 1.5 mM).

We investigated both of these compounds for their ability to precipitate oxalate and terephthalate: while **3·Cl$_2$** is not a practical oxalate precipitant due to its limited aqueous solubility, it is remarkably effective at precipitating these anions, with precipitation observed at concentrations as low as 0.020 mM for terephthalate and 0.050 mM for oxalate. To investigate the role of precipitant solubility and the importance of packing efficiency, we prepared **3_{OMe}·Cl$_2$**, where two methoxy groups were added to the central ring of the terphenyl precipitant. Unfortunately, this compound had poor solubility properties and so was not investigated further (see SI for synthesis).

Benzene bis-amidinium 2^{2+} is less effective than 1^{2+} as a precipitant, but shows relatively high precipitation efficiency and can precipitate oxalate at 1.0 mM and terephthalate at 0.25 mM, which is noteworthy given its very high water solubility (~ 150 mM). To try and gain insight into the precipitation properties of 2^{2+} and allow comparisons with 1^{2+}, we report the X-ray crystal structures of **2·oxalate** and **2·sulfate** and compare these with the previously-reported[46] structure of **2·terephthalate** (Figure 4). These three structures, **2·oxalate**, **2·sulfate** and **2·terephthalate** are anhydrous and quite densely packed (KPIs: 0.71 – 0.77 crystal densities: 1.48 – 1.52 g cm^{-3}), and these parameters are generally very similar to the analogous structures containing **1^{2+}**, except that **1·sulfate** has an anomalously low KPI, as previously discussed.

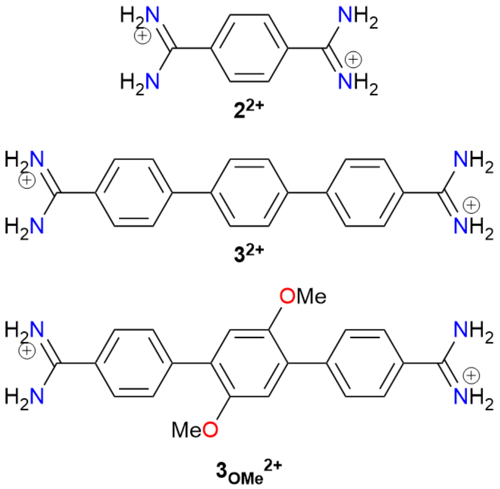


Figure 3 Other bis-amidinium precipitants investigated.

Hydrogen bonding arrangements in **2·oxalate**, **2·sulfate** and **2·terephthalate** are similar to those seen in **1·carbonate**, **1·oxalate**, **1·succinate**, **1·sulfate** and **1·terephthalate**, although in **2·oxalate** the oxalate anion is rotated 90° relative to its orientation in **1·oxalate**. For a given anion, the smaller precipitant **2^{2+}** forms slightly shorter hydrogen bonds in each case, although these differences are very small. In any case, it is clear that the lower solubility of carboxylate/sulfate complexes of **1^{2+}** is not due to a significantly tighter hydrogen bonding arrangement.

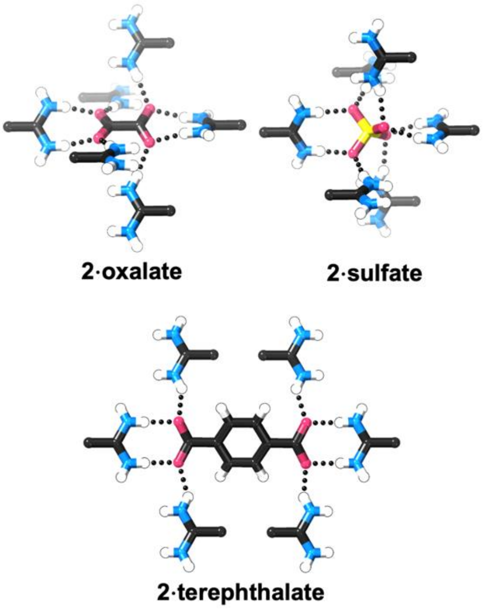


Figure 4 Portions of X-ray crystal structures showing hydrogen bonding arrangements around anion in **2·oxalate**, **2·sulfate** and **2·terephthalate**. The structure of **2·terephthalate** has been reported previously.[46] These hydrogen bonding arrangements are very similar to the analogous structures containing **1^{2+}** instead of **2^{2+}** (Figure 3).

Conclusions

Bis-amidinium **1^{2+}** is a highly effective precipitant for oxalate and terephthalate, even at sub-millimolar concentrations. It is selective over other polycarboxylate anions and divalent CO_3^{2-}, HPO_4^{2-} and SO_4^{2-}. Crystallisation is both enthalpically and entropically favourable, with the entropic component presumably arising from an increase in disorder of the system when the large and ordering biphenyl molecule is removed from water. Interestingly, analysis of the crystal structures of nine salts of **1^{2+}** and three of the smaller bis-amidinium **2^{2+}** does not reveal any direct trends between solubility and either packing density or hydrogen bond length. However, it is notable that all the least soluble materials are anhydrous and have eight amidinium N–H groups forming short charge-assisted hydrogen bonds to the anion. This work demonstrates that it is possible to selectively precipitate certain dicarboxylates, expanding on pioneering work from the Custelcean group investigating precipitants for sulfur/selenium based anions.[23–25] It is hoped that this work will lead to the development of selective precipitants for a wide range of toxic or damaging anions.

Experimental Section

General remarks

The bis-amidinium **1·Cl$_2$** was purchased from Ambeed; it can also be readily prepared from the corresponding dinitrile.[26] Bis-amidinium compounds **2·Cl$_2$**[47] and **3·Cl$_2$**[26] were prepared from the corresponding dinitriles as previously described; the synthesis of **3$_{OMe}$·Cl$_2$** is given in the SI. Anions were used as their sodium salts; all of these were commercially-available, apart from sodium terephthalate, which was prepared from terephthalic acid as described previously,[48] and then recrystallised from water/acetone. Details of characterisation of all new compounds and frameworks are provided in the Supporting Information.

Data availability statement

Crystallographic data for **1·(ClO$_4$)$_2$**, **1$_{1.5}$·citrate**, **1·malonate**, **1·oxalate**, **1·succinate**, **1·terephthalate**, **2·oxalate** and **2·sulfate** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers 2326321 – 2326328. Crystal data for **1·Cl$_2$** (CCDC: 2222090), **1·carbonate** (CCDC: 2222092), **1·sulfate** (CCDC: 2222091) and **2·terephthalate** (CCDC: 2047427) have previously been deposited with the CCDC. Other data are provided in the SI.

Acknowledgements

We thank the Australian Research Council (DP170100118 to KAJ, FT210100495 to NGW) and an ANU Research School of Chemistry *Environment and Sustainability* grant for funding. We thank Dr Dan Preston (ANU) for assistance with understanding van't Hoff analyses.

References

(1) Beer, P. D.; Gale, P. A. Anion Recognition and Sensing: The State of the Art and Future Perspectives. *Angew. Chem. Int. Ed.* **2001**, *40* (3), 486–516.

(2) Gale, P. A.; Caltagirone, C. Anion Sensing by Small Molecules and Molecular Ensembles. *Chem. Soc. Rev.* **2015**, *44* (13), 4212–4227.

(3) Williams, G. T.; Haynes, C. J. E.; Fares, M.; Caltagirone, C.; Hiscock, J. R.; Gale, P. A. Advances in Applied Supramolecular Technologies. *Chem. Soc. Rev.* **2021**, *50* (4), 2737–2763.

(4) Langton, M. J.; Serpell, C. J.; Beer, P. D. Anion Recognition in Water: Recent Advances from a Supramolecular and Macromolecular Perspective. *Angew. Chem. Int. Ed.* **2016**, *55* (6), 1974–1987.

(5) Park, C. H.; Simmons, H. E. Macrobicyclic Amines. III. Encapsulation of Halide Ions by in,in-1,(k + 2)-Diazabicyclo[k.l.m.]Alkane Ammonium Ions. *J. Am. Chem. Soc.* **1968**, *90* (9), 2431–2432.

(6) Schmidtchen, F. P. Inclusion of Anions in Macrotricyclic Quaternary Ammonium Salts. *Angew. Chem. Int. Ed. Engl.* **1977**, *16* (10), 720–721.

(7) Kubik, S.; Goddard, R.; Kirchner, R.; Nolting, D.; Seidel, J. A Cyclic Hexapeptide Containing L-Proline and 6-Aminopicolinic Acid Subunits Binds Anions in Water. *Angew. Chem. Int. Ed.* **2001**, *40* (14), 2648–2651.

(8) Zhou, H.; Zhao, Y.; Gao, G.; Li, S.; Lan, J.; You, J. Highly Selective Fluorescent Recognition of Sulfate in Water by Two Rigid Tetrakisimidazolium Macrocycles with Peripheral Chains. *J. Am. Chem. Soc.* **2013**, *135* (40), 14908–14911.

(9) Langton, M. J.; Robinson, S. W.; Marques, I.; Felix, V.; Beer, P. D. Halogen Bonding in Water Results in Enhanced Anion Recognition in Acyclic and Rotaxane Hosts. *Nat Chem* **2014**, *6* (12), 1039–1043.

(10) Yawer, M. A.; Havel, V.; Sindelar, V. A Bambusuril Macrocycle That Binds Anions in Water with High Affinity and Selectivity. *Angew. Chem. Int. Ed.* **2015**, *54* (1), 276–279.

(11) Liu, Y.; Zhao, W.; Chen, C.-H.; Flood, A. H. Chloride Capture Using a C–H Hydrogen-Bonding Cage. *Science* **2019**, *365* (6449), 159–161.

(12) Sudan, S.; Chen, D.; Berton, C.; Fadaei-Tirani, F.; Severin, K. Synthetic Receptors with Micromolar Affinity for Chloride in Water. *Angew. Chem. Int. Ed.* **2023**, *62* (9), e202218072.

(13) Sivalingam, V.; Krishnaswamy, S.; Chand, D. K. A Template-Free Pd2L4 Cage with up to Nanomolar Affinity for Chloride in Aqueous Solutions. *Chem. Eur. J.* **2023**, *29* (33), e202300891.

(14) Jing, L.; Deplazes, E.; Clegg, J. K.; Wu, X. A Charge-Neutral Organic Cage Selectively Binds Strongly Hydrated Sulfate Anions in Water. *Nat. Chem.* **2024**, *16*, 335–342.

(15) Kubik, S.; Kirchner, R.; Nolting, D.; Seidel, J. A Molecular Oyster: A Neutral Anion Receptor Containing Two Cyclopeptide Subunits with a Remarkable Sulfate Affinity in Aqueous Solution. *J. Am. Chem. Soc.* **2002**, *124* (43), 12752–12760.

(16) Mittapalli, R. R.; Namashivaya, S. S. R.; Oshchepkov, A. S.; Kuczyńska, E.; Kataev, E. A. Design of Anion-Selective PET Probes Based on Azacryptands: The Effect of pH on Binding and Fluorescence Properties. *Chem. Commun.* **2017**, *53* (35), 4822–4825.

(17) Wu, Y.; Zhang, C.; Fang, S.; Zhu, D.; Chen, Y.; Ge, C.; Tang, H.; Li, H. A Self-Assembled Cage Binding Iodide Anion over Halide Ions in Water. *Angew. Chem. Int. Ed.* **2022**, *61* (38), e202209078.

(18) Samanta, J.; Tang, M.; Zhang, M.; Hughes, R. P.; Staples, R. J.; Ke, C. Tripodal Organic Cages with Unconventional CH-O Interactions for Perchlorate Remediation in Water. *J. Am. Chem. Soc.* **2023**, *145* (40), 21723–21728.

(19) Moyer, B. A.; Custelcean, R.; Hay, B. P.; Sessler, J. L.; Bowman-James, K.; Day, V. W.; Kang, S.-O. A Case for Molecular Recognition in Nuclear Separations: Sulfate Separation from Nuclear Wastes. *Inorg. Chem.* **2013**, *52* (7), 3473–3490.

(20) Belcher, R.; Nutten, A. J. 114. Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part I. Solubilities of the Sulphates. *J. Chem. Soc.* **1951**, 544–546.

(21) Belcher, R.; Nutten, A. J.; Stephen, W. I. 274. Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part XII. Reagents for the Precipitation of Sulphate. *J. Chem. Soc.* **1953**, 1334–1337.

(22) Stephen, W. I. A New Reagent for the Detection and Determination of Small Amounts of the Sulphate Ion. *Anal. Chim. Acta* **1970**, *50* (3), 413–422.

(23) Custelcean, R.; Williams, N. J.; Seipp, C. A. Aqueous Sulfate Separation by Crystallization of Sulfate–Water Clusters. *Angew. Chem. Int. Ed.* **2015**, *54* (36), 10525–10529.

(24) Custelcean, R.; Williams, N. J.; Seipp, C. A.; Ivanov, A. S.; Bryantsev, V. S. Aqueous Sulfate Separation by Sequestration of [(SO4)2(H2O)4]4− Clusters within Highly Insoluble Imine-Linked Bis-Guanidinium Crystals. *Chem. Eur. J.* **2016**, *22* (6), 1997–2003.

(25) Einkauf, J. D.; Williams, N. J.; Seipp, C. A.; Custelcean, R. Near Quantitative Removal of Selenate and Sulfate Anions from Wastewaters by Cocrystallization with Chelating Hydrogen-Bonding Guanidinium Ligands. *JACS Au* **2023**, 3 (3), 879–888,

(26) Tzioumis, N. A.; Cullen, D. A.; Jolliffe, K. A.; White, N. G. Selective Removal of Sulfate from Water by Precipitation with a Rigid Bis-Amidinium Compound. *Angew. Chem. Int. Ed.* **2023**, *62* (12), e202218360.

(27) Curiel, D.; Más-Montoya, M.; Sánchez, G. Complexation and Sensing of Dicarboxylate Anions and Dicarboxylic Acids. *Coord. Chem. Rev.* **2015**, *284*, 19–66.

(28) Butler, S. M.; Jolliffe, K. A. Molecular Recognition and Sensing of Dicarboxylates and Dicarboxylic Acids. *Org. Biomol. Chem.* **2020**, *18* (41), 8236–8254.

(29) Tang, L.; Park, J.; Kim, H.-J.; Kim, Y.; Kim, S. J.; Chin, J.; Kim, K. M. Tight Binding and Fluorescent Sensing of Oxalate in Water. *J. Am. Chem. Soc.* **2008**, *130* (38), 12606–12607.

(30) Akdeniz, A.; Caglayan, M. G.; Anzenbacher, P. A Tri-Serine Tri-Lactone Scaffold for the Quantification of Citrate in Urine. *Chem. Commun.* **2016**, *52* (9), 1827–1830.

(31) Lehn, J.-M.; Méric, R.; Vigneron, J.-P.; Bkouche-Waksman, I.; Pascard, C. Molecular Recognition of Anionic Substrates. Binding of Carboxylates by a Macrobicyclic Coreceptor and Crystal Structure of Its Supramolecular Cryptate with the Terephthalate Dianion. *J. Chem. Soc. Chem. Commun.* **1991**, No. 2, 62–64.

(32) Mateus, P.; Delgado, R.; André, V.; Duarte, M. T. Dicarboxylate Recognition Properties of a Dinuclear Copper(II) Cryptate. *Inorg. Chem.* **2015**, *54* (1), 229–240.

(33) Cheng, K. Y.; Mohottige, T. W.; Ginige, M. P.; Kaksonen, A. H. New Perspectives for Bio-Technical Treatment of Oxalate-Containing Waste Streams from Bauxite Processing. *Hydrometallurgy* **2023**, *220*, 106105.

(34) Schuler, E.; Demetriou, M.; Shiju, N. R.; Gruter, G.-J. M. Towards Sustainable Oxalic Acid from CO2 and Biomass. *ChemSusChem* **2021**, *14* (18), 3636–3664.

(35) Breunig, H. M.; Rosner, F.; Lim, T.-H.; Peng, P. Emerging Concepts in Intermediate Carbon Dioxide Emplacement to Support Carbon Dioxide Removal. *Energy Environ. Sci.* **2023**, *16* (5), 1821–1837.

(36) Barnard, E.; Rubio Arias, J. J.; Thielemans, W. Chemolytic Depolymerisation of PET: A Review. *Green Chem.* **2021**, *23* (11), 3765–3789.

(37) Yu, L.-J.; Cullen, D. A.; Morshedi, M.; Coote, M. L.; White, N. G. Room Temperature Hydrolysis of Benzamidines and Benzamidiniums in Weakly Basic Water. *J. Org. Chem.* **2021**, *86* (19), 13762–13767.

(38) Rumble, J. R.; Bruno, T. J.; Doa, M. J. *CRC Handbook of Chemistry and Physics, 102nd Edition*; CRC Press, 2021.

(39) Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Crystallogr.* **2015**, *C71*, 9–18.

(40) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press, 1973.

(41) Spek, A. Single-Crystal Structure Validation with the Program PLATON. *J. Appl. Crystallogr.* **2003**, *36* (1), 7–13.

(42) Thompson, A. L.; White, N. G. Hydrogen Atoms in Supramolecular Chemistry: A Structural Perspective. Where Are They, and Why Does It Matter? *Chem. Soc. Rev.* **2023**, *52*, 6254–6269.

(43) Default N–H restraints were used within the CRYSTALS suite. For amidinium groups these are that the N–H bond should be 0.86(2) Å in length and the C–N–H angle should be 120(2)°. The actual N–H distances after refinement ranged from 0.828 to 0.907 Å, with a mean Value of 0.874(2) Å. Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout. K.; Watkin, D. J. CRYSTALS Version 12: Software for Guided Crystal Structure Analysis. *J. Appl. Crystallogr.* **2003**, *36* (6), 1487.

(44) Alvarez, S. A Cartography of the van Der Waals Territories. *Dalton Trans.* **2013**, *42* (24), 8617–8636.

(45) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Definition of the Hydrogen Bond (IUPAC Recommendations 2011). **2011**, *83* (8), 1637–1641.

(46) Nicks, J.; Boer, S. A.; White, N. G.; Foster, J. A. Monolayer Nanosheets Formed by Liquid Exfoliation of Charge-Assisted Hydrogen-Bonded Frameworks. *Chem. Sci.* **2021**, 12, 3322–3327.

(47) Wang, K.; Yang, L.-M.; Wang, X.; Guo, L.; Cheng, G.; Zhang, C.; Jin, S.; Tan, B.; Cooper, A. Covalent Triazine Frameworks via a Low-Temperature Polycondensation Approach. *Angew. Chem. Int. Ed.* **2017**, *56* (45), 14149–14153.

(48) Zaltariov, M.-F.; Vlad, A.; Cazacu, M.; Shova, S.; Balan, M.; Racles, C. A Novel Siloxane-Containing Dicarboxylic Acid, 1,3-Bis(p-Carboxyphenylene-Ester-Methylene)Tetramethyldisiloxane, and Its Derivatives: Ester Macrocycle and Supramolecular Structure with a Copper Complex. *Tetrahedron* **2014**, *70* (16), 2661–2668.